

The effect of a free radical quencher on the conductivity, oxidative stability and free radical population of poly(1,6-heptadiyne)

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The effect of a free radical quencher on the intrinsic properties of poly(1,6-heptadiyne) has been studied. It is shown that this treatment reduces the number of free radicals, lowers the conductivity while leaving the transport barriers unchanged and reduces the susceptibility of the material to oxidation. These effects are discussed in terms of hydrogen atom transfer chemistry.

Keywords Conduction; oxidation; stabilization; poly(1,6-heptadiyne); spin populations

INTRODUCTION

Polyacetylene^{1,2} (PAC) and its derivatives such as poly(1,6-heptadiyne)³⁻⁵ (P-1,6) and polymethylacetylene⁶ have been intensely studied over the past few years because of the ability to dope these materials to metallic-like conductivity. The intrinsic conductivity has been reported as $\sim 10^{-5}$ (ohm-cm)⁻¹ for *trans* PAC, 10^{-9} (ohm-cm)⁻¹ for *cis* PAC⁷, for 10^{-12} (ohm-cm)⁻¹ for P-1,6³, $\sim 10^{-9}$ (ohm-cm)⁻¹ for polymethylacetylene⁶. E.s.r. measurements indicate free spin populations in PAC ($g \sim 2$) of $\sim 10^{19}$ spins/gm. These results have been interpreted in terms of either electrons excited to the conduction band in these large gap semiconductors, or intrinsic defects via deviations from a pure bond alternation conformation⁸. Such a defect structure for PAC is shown in *Figure 1*. These positions, as well as those CH₂ groups adjacent to the double bonds in P(1,6) (see *Figure 1b*) and poly(methylacetylene), are allylic⁹.

P-1,6 contains four allylic hydrogen atoms for each monomer unit as compared with PAC in which defects cannot be associated with each monomer unit, but with a possible structural variation formed during or more probably after polymerization during the *cis*→*trans* isomerization. Because of this proximity to the polyene double bonds, highly delocalized free radicals can easily form by the loss of a hydrogen atom⁹ (see *Figure 1*). When this occurs a neutral 'soliton' is formed. This soliton is the basis for the defect model of conductivity in these systems^{10,11}. Doping such systems with electron withdrawing materials is believed to remove the free radical and provide for hole conduction in the polyene. Doping with an electron donor would add an electron and provide for electron conduction¹². The stable allylic free radical formed would also provide a position for the addition of oxygen, leading to degradation of the polyene materials¹³⁻¹⁷.

We have undertaken a study of the effect of the free

radical quencher Tinuvin 770^{R†} (hereafter 770) on the intrinsic conductivity of P-1,6. The partial structure of 770 is shown in *Figure 2*. The H-atom attached to the nitrogen atom in such a structure is extremely labile and is believed to be able to transfer to the allylic free radical positions of P-1,6 when brought in intimate contact with them. This experiment is different from donor doping of PAC. In those experiments an electron is transferred to the polyene forming an anion. In this case a neutral hydrogen atom is transferred to the polymer. The following reports the effect of such treatment on the intrinsic conductivity, oxidative stability and free radical population of P(1,6).

EXPERIMENTAL

Samples of pentane-washed and toluene-washed P-1,6 were swelled in: (1) pure degassed benzene or toluene, and (2) in various concentrations (gms/ml) of Tinuvin 770/degassed benzene solutions (see *Figures*). Both solvents cause the polymer to become plasticized and highly elastic. The samples were then washed with degassed benzene and vacuum dried at 10^{-5} mm Hg for 48 h prior to any electrical measurements.

Electrical measurements were made *via* the two probe technique with contacts of stainless steel and solder, which provide ohmic contacts in the voltage range used. The sample was placed in series with a Keithley regulated voltage supply and a Keithley 616 electrometer. The sample was maintained in a cell through which thermally regulated argon was circulated to prevent oxidation. Temperature was controlled with a Delta Design Environmental oven ($\pm 1^\circ\text{C}$), and monitored with a thermocouple mounted within one cm of the sample. Data was recorded in the scanning mode at 1K min^{-1} . Oxidation experiments were conducted by replacing the flowing argon with pure oxygen and monitoring current as a function of time. E.s.r. experiments were conducted on a Varian E109 e.s.r. spectrometer operating at a frequency of $\sim 9.5\text{ GHz}$ and power levels of 1 to 10 mW. E.s.r. samples were made by vacuum sealing (10^{-5} mm

† Registered trademark of Ciba Geigy

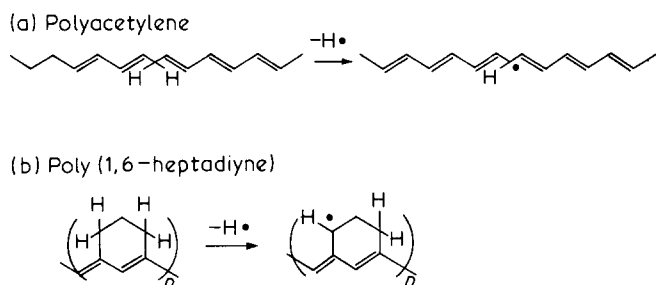


Figure 1 (a) Defect structure and free radical form of polyacetylene. (b) Chemical structure and free radical form of poly(1,6-heptadiyne)

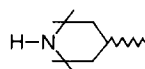


Figure 2 Partial chemical structure of Tinuvin 770

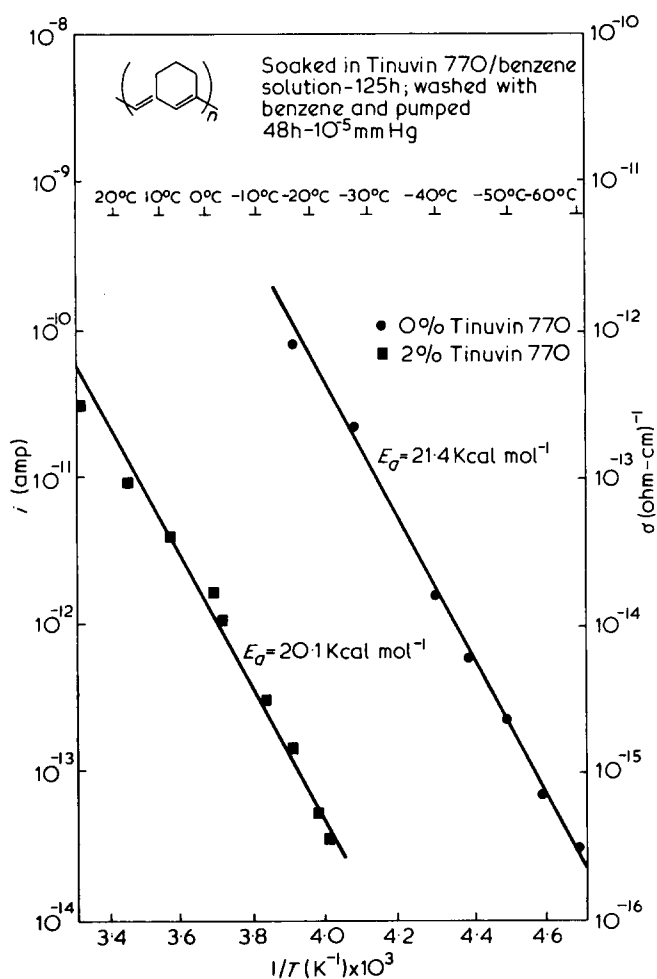


Figure 3 Log conductivity (ohm-cm)⁻¹ versus inverse temperature for a pentane washed P(1,6) sample treated as shown in the figure. $E \approx 2V/\mu M$

Hg) each sample in an e.s.r. tube. Care was taken to avoid any oxygen contamination during the preparative process by using an oxygen free (<0.8 PPM) glove box.

RESULTS AND DISCUSSION

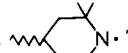
Conductivity

The time dependent chemical nature of P(1,6) has been discussed previously¹⁶. In that work it was shown that not only solvent wash, but time after solvent wash can affect

the properties of P(1,6). The work reported here is, therefore, always presented with a reference material. The results of two sets of experiments are shown in Figures 3 and 4. Addition of the radical quencher lowers conductivity, while the activation energy (calculated from $\log \sigma = \log \sigma_0 - E_a/KT$) remains constant. Unfortunately, the two P(1,6) samples used in the experiments were prepared differently (one was washed with pentane and the other with toluene to remove catalyst). As seen in the data this appears to yield materials of different activation energies. Within the series, however, data was reproducible. Since there is evidence that washing with solvents such as benzene can remove additional material from a previously washed sample¹⁶, it appears that removal of this material increases the transport barrier in P(1,6). The addition of 770 reduces the product of n (number of charge carriers) and μ (mobility), i.e., a decrease in conductivity, but the transport barrier is unchanged.

E.s.r.

The e.s.r. spectra of these materials provide information on the relative spin population of the various samples. The 770 solid state spectrum shown in Figure 5 is the nitrogen spin coupled triplet of the stable free radical. A

portion of the material thus exists as . The e.s.r.

spectrum of the P(1,6) sample used in Figure 3 is as shown in Figure 6 a singlet with $\Delta H \sim 20$ G. The linewidth is much broader than that observed in well annealed samples of *trans*-polyacetylene^{11,17} and is indicative of more localized spins than in the polyacetylene case^{17,18}.

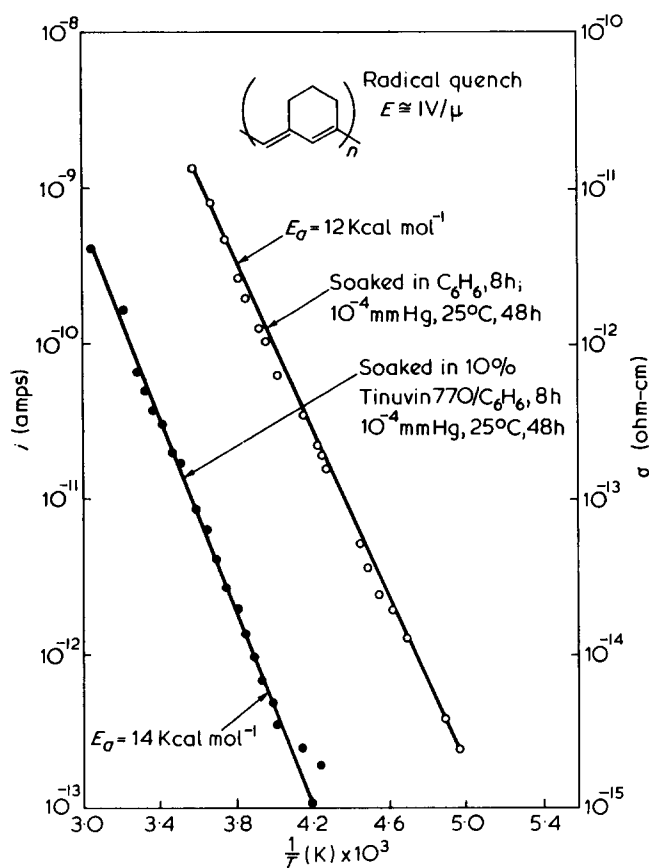


Figure 4 Log conductivity (ohm-cm)⁻¹ versus inverse temperature for a toluene washed P(1,6) sample treated as shown in the figure.

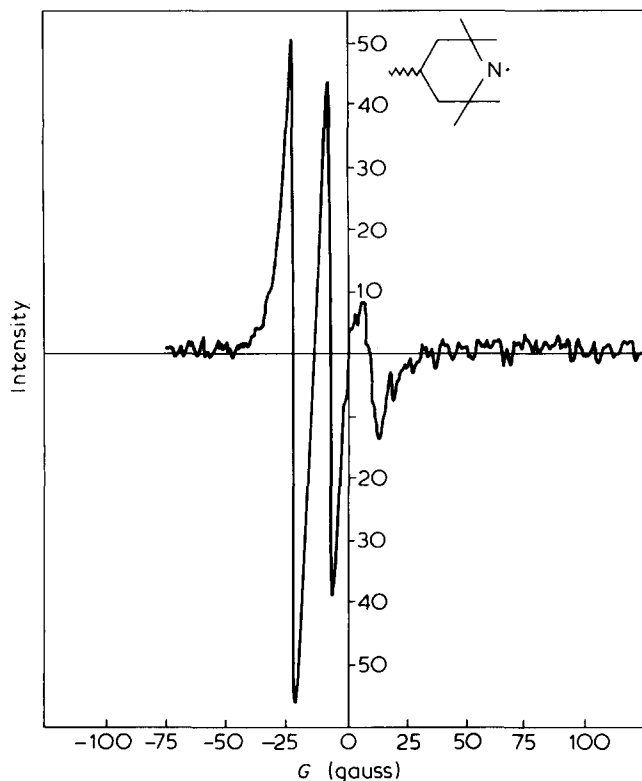


Figure 5 E.s.r. spectrum for solid Tinuvin 770. Field set is 3365 G with microwave power at 10 mW

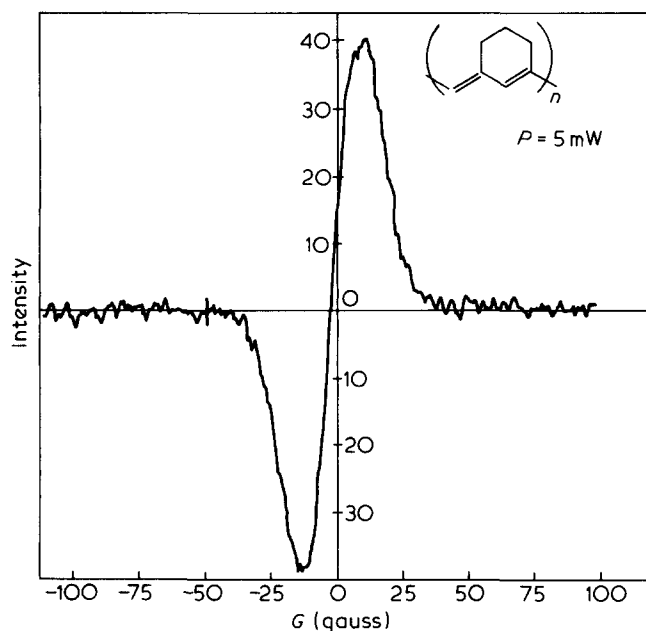
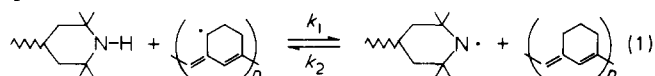


Figure 6 E.s.r. spectrum for benzene washed sample of Figure 3. Field set equals 3354 G. Microwave power equals 5 mW

We have noted no saturation effects in the 0.5 to 10.0 mW power range. In the 770 treated sample the triplet spectrum of 770 was not observed, indicating that very little of the 770 free radical was present or that very little 770 remained on the sample. The observed linewidth was identical to that of the material not treated with 770. A comparison of the spin intensities for the 770 treated and untreated samples indicates that at 125 h exposure to the 770 a decrease of spin population of a factor of 2 or less causes the observed changes in conductivity. This is not unreasonable since we have shown that in *trans*-

polyacetylene an order of magnitude change in the free spin population results in eight orders of magnitude change in conductivity¹⁸.

Since the reaction of 770 with P(1,6) is an equilibrium process, i.e.,



it might be expected that changing the 770 treatment conditions would affect the observed results. This was studied by changing treatment after exposure to 770. In one case samples were withdrawn from the 770 and dried. The other samples were washed with degassed benzene prior to drying. In all cases the benzene washed samples exhibited higher spin counts than their unwashed counterpart. The experiment indicates that the equilibrium picture above is correct and that reducing the 770 concentration in the polymer drives the reaction to the left.

Oxidative stability

The population of free radicals should also affect the oxidative stability of the polyenes, since triplet oxygen insertion at a localized free radical position is facile¹⁸. Therefore, the oxidative stability of the P(1,6) samples treated with various concentrations of 770 solution was studied. Monitoring the conductivity as oxidation takes place yields first order kinetics in that plots of $\log i$ (or

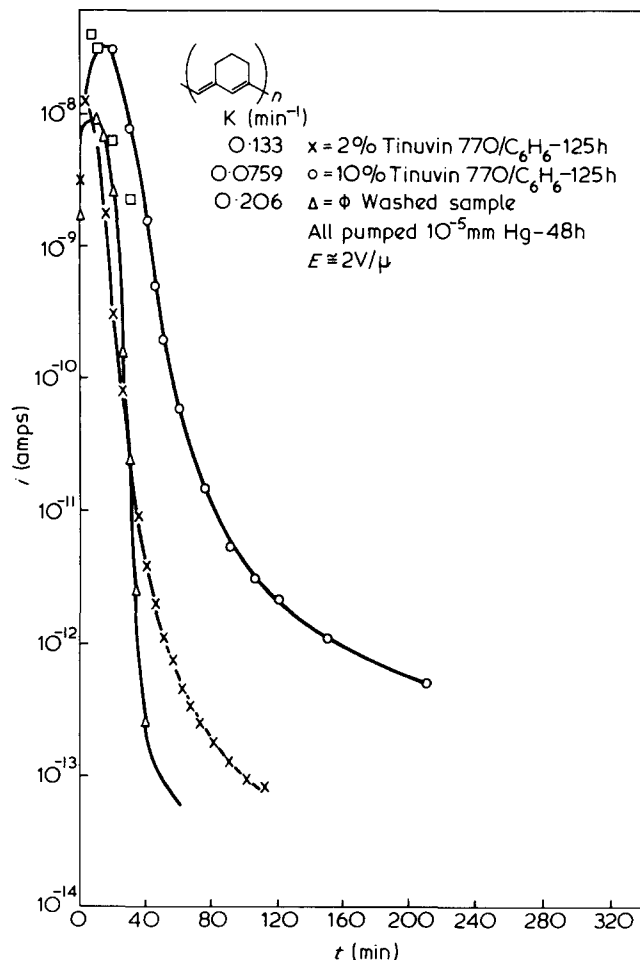


Figure 7 Log i versus exposure time to oxygen for P(1,6) samples exposed to benzene solutions with various Tinuvin^R 770 concentrations for 125 h, washed 1 min in benzene and dried at 10^{-5} mm Hg for 48 h. Temperature ≈ 321 K

conductivity) versus time provide straight line decreases after an initial increase associated with doping¹⁶. The data in Figure 7 is a comparison of the oxidation of the various treated samples. Two points are obvious: (1) the initial decay rate decreases as the 770 concentration increases; (2) the time needed for complete degradation increases with increasing 770 concentration. The data indicate that replacing the free radical with hydrogen stabilizes the polymer to oxidation. The increase in stability with increasing 770 concentration further indicates that equation 1 is a valid picture of the chemistry taking place during quenching.

With polyacetylene we have found that the inability of benzene to swell the polymer precludes its stabilization to oxidation by this technique.

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